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(ACCESSION NUMBER)

52

(PAGES)

CR-58503

(NASA CR OR TMX OR AD NUMBER)

(THRU)

(CODE)

07

(CATEGORY)

OTS PRICE

XEROX

\$

5.60

MICROFILM

\$

07

ANNUAL REPORT
ELECTROLYTIC PREPARATION
OF
HIGH DIELECTRIC THIN FILMS

by

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4-55-64-1

27 June 1963 - 27 June 1964

Work carried out under NASw 765 for the
Office of Advanced Research and Technology,
NASA Headquarters, Washington 25, D. C.

Research Laboratories
LOCKHEED MISSILES & SPACE COMPANY
A Group Division of Lockheed Aircraft Corporation
Palo Alto, California

FOREWORD

The work described in this report was carried out under contract NASw 765 for the NASA Headquarters, Washington 25, D.C. The program was directed toward the development of high dielectric thin films prepared by electrolytic techniques.

Acknowledgment is made to R. D. Wales, J. B. Story, S. A. Ring, and B. A. Traina for their contribution to the process development and literature survey portions of this study.

ABSTRACT

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The preparation of high dielectric thin films is described and the results are compared and interpreted with the results reported by others working this area. It has been shown that a secondary oxide can be deposited in a simultaneously formed oxide film by electrolytic conversion methods. However, it is doubtful that doping the film with small amounts of secondary oxides by use of normal anodization techniques produces any major improvement in electrical characteristics. This is quite probably due to the amorphous nature of the normal anodic films. Deposition of dispersed high dielectric material on the anode has been accomplished.

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Section 1 INTRODUCTION

The problem prompting this program concerns the need for microminiature capacitive elements in thin film form for use in integrated circuitry. Presently developed thin film capacitive elements are largely amorphous structures of relatively low dielectric constant and require large areas to obtain significant capacitance levels. The objective of this program is to develop procedures for the deposition of high dielectric materials on suitable ceramic-metal substrates in thin film form to provide structures as capacitive elements. Capacity values on the order of 2 to 5 $\mu\text{f}/\text{cm}^2$ is a goal of this research.

The scope of the program includes a study of the parameters concerned in electrolytic film formation and an evaluation of the films produced. The basic approach proposed for the preparation of these high-capacity elements entails the formation of a porous oxide film coupled with the deposition of a second phase so as to produce a double-oxide composition. The porous oxide film is to be prepared electrolytically by anodization of a suitable metal substrate. The second phase is to be physically occluded in the porous film by the entrapment of ionic or finely particulate species during the anodization. Electrophoretic processes may be employed as an aid in achieving deposition of the second phase. An alternate approach would involve anodization of a suitable metal-alloy substrate to produce directly a composite oxide structure. The choice of metal substrate and addition agents – and therefore of the final composite oxide – will be governed by the presently available information on high dielectric compounds prepared by conventional ceramic techniques. Assuming dielectric constants on the order of 500 to 2,000, capacity values of 2 to 5 $\mu\text{f}/\text{cm}^2$ may be attainable for the thin films.

The development of an all-film circuit would offer increased component density, greater reliability, further design versatility, and simplified production techniques, and would eliminate the necessity of wired semiconductor and high dielectric elements separate from the integrated circuit.

Section 2

LITERATURE SURVEY

The recent literature related to this project was approached through a search of Chemical Abstracts from January 1957 through June 1962. The search covered the oxygen-containing compounds of barium, calcium, cadmium, cobalt, copper, iron, magnesium, nickel, strontium, and zinc which also contain titanium, zirconium, niobium, or tantalum. The list of references so obtained was extensive. Since a complete treatment of the list is not needed and could not be justified, a representative cross section of research in this period was made by using the years 1957, 1960, and January to June 1962. The references for these years were considered in further detail, and the most promising (approximately 100) selected. In this survey it became apparent that one author, Smolenskii, was outstanding. A complete survey was made on his work, and that of his principal coworker, Isupov. The references are listed in Section 5.

The principal distinctive peculiarity of ferroelectrics is the presence of a phase transition of the first or second order from a disordered state into a well-ordered, polarized state (Ref. 1).

As a result of this spontaneous polarization, the ferroelectrics possess more pronounced anomalies in the electrical and other properties than do most ionic crystals. At temperatures below the phase transition, the ferroelectrics show spontaneous deformations and a reduction of lattice symmetry (Ref. 1).

The appearance of spontaneous polarization can be explained within the framework of the classical electrostatic interaction, since the internal field is determined by the reciprocal action of the dipoles which, in turn, are conditioned by a displacement of ions. An essential role is played not only by the long-range (dipole) forces, but also by short-range forces. Spontaneous polarization arises only when the elastic

component of the restoration force occurring during a displacement of ions is less than the dipole forces (Ref. 1).

Ferroelectrics and antiferroelectrics may be divided into two groups, depending upon whether or not they contain hydrogen. The first group, containing hydrogen, includes potassium sodium tartrate (Seignette salt or Rochelle salt), phosphates and arsenates of potassium, and others. The second group, not containing hydrogen, includes barium titanate, lead titanate, potassium niobate, and others. This second group is characterized by the fact that each cation is within an oxygen octahedron, and all or part of the cations have the electronic structure of a noble gas atom after giving up s and d electrons. The charge should be large and the ionic radius small (Ref. 2).

In a typical ferroelectric substance of the oxyoctahedral type, such as BaTiO_3 , there is a marked change in the dielectric constant with temperature, with an exceedingly high dielectric constant being observed within a narrow range. Each substrate usually (but not always) has a single maximum lying between -200° and $+400^\circ \text{C}$. The temperatures of these maxima and the breadth of the peak are commonly changed by the addition of a second substance. When a peak is broadened, it is usually lowered.

A number of compositions having high dielectric constants at room temperature have been selected from the literature and are presented in Table 2-1.

A reference closely related to the present project is that of Maxwell (Ref. 3). He formed a capacitor from titania containing 1 percent by weight antimony oxide. This small amount of antimony makes the TiO_2 conducting. This conductivity has been attributed to substitution of Sb^{5+} ions for some Ti^{4+} ions, resulting in Ti^{3+} ions and electrons free to move in the lattice as in n-type semiconductors. When electrodes are fired onto a conductive TiO_2 body, thin insulating layers on the surfaces of the body and a complete capacitor are produced simultaneously. The capacitor is of the layerized type. The equivalent circuit consists of two condensers in series with, and separated by, a resistance. Each of the condensers is also in parallel with a high resistance. This means that the effective capacitance occurs in thin layers at the two surfaces of the titania. This close spacing allows an increase in the effective dielectric

Table 2-1
DIELECTRIC CONSTANTS OF HIGH DIELECTRIC CERAMIC MATERIALS (K > 500)

Material (System)	Dielectric Properties at 25° C		Curve With Minimum Dielectric Constant				
	Frequency (cps)	K	Temp. at Max. (° C)	K Max.	Lower Limit for K=500 (° C)	Upper Limit for K=500 (° C)	Refs.
BaTiO ₃	1 m	1,143	120	5,100	-10	170	3, 4
Ba _{0.7} Sr _{0.3} TiO ₃	1 k	2,000	70	12,000	-100	100	5
Ba _{0.7} Pb _{0.3} TiO ₃		5,200	15	6,500			4
Bi _{0.5} K _{0.5} TiO ₃	500 k	600	390	3,400	25	450	6
CaTiO ₃	1 m	1,677					3
CdTiO ₃	1 m	1,600	60	1,600	60	120	7
(Ba,Pb)(TiS _n)O ₃		5,000					3
Semiconducting Barrier Layer Titanates, Such as							
(Ba,Sr)TiO _{3-x}		500,000					3
BaTi _{0.85} Sn _{0.15} O ₃	500 k	11,500	20	14,000	-70	150	4
BaTi _{0.85} Zr _{0.15} O ₃	500 k	1,000	65	9,000	-5	100	4
(Ba,Pb)ZrO ₃		6,000					3
NaNbO ₃		500					3
KNbO ₃		700					3
Ba _{0.4} Pb _{0.6} Nb ₂ O ₆	1 k	1,100	300	5,500	0	400	8
Ba _{0.25} Sr _{0.25} Pb _{0.5} Nb ₂ O ₆	1 k		120	6,500	-50	400	8
Pb ₂ FeNbO ₆	300 k	1,300	110	5,500	-100	250	9
Pb ₃ MgNb ₂ O ₉	1 k	8,000	-10	13,000	-150	100	10
(Na,Cd)NbO ₃	1 m	1,000					3
NaNbO ₃ -Sr ₂ Ta ₂ O ₇	1 k	2,600					3

constant from about 100 to 10,000 (for specimens 0.04-in. thick). It was found that these capacitors had a flat temperature characteristic.

A second reference of interest to the present project is that of Herczog (Ref. 11). He formed capacitors of BaTiO_3 in the feldspar, $\text{BaAl}_2\text{Si}_2\text{O}_8$, by heat treatment of glasses with compositions corresponding to $X\text{BaTiO}_3 + (100-X)\text{BaAl}_2\text{Si}_2\text{O}_8$. The BaTiO_3 content and particle size of the microcrystalline product could be easily controlled by the conditions of heat treatment and the glass composition. The electrical properties of the microcrystalline product were described in terms of the BaTiO_3 content and primarily the particle size. Herczog found that surface effects predominate in materials with particle sizes less than 0.2μ , the dielectric constant is independent of temperature, and ferroelectric behavior is degenerate. In material with BaTiO_3 particle sizes between 0.2 and 1μ , the electrical properties are the result of contributions from both surface and normal bulk properties. The two contributions are equal at about 1μ where the dielectric constant is the highest for all particle sizes. Other unusual electrical properties are due to the mechanical clamping of the BaTiO_3 in the pore-free matrix.

Section 3

EXPERIMENTAL RESULTS AND DISCUSSION

3.1 APPROACH

The general experimental approach to the preparation and evaluation of potential high dielectric thin films has been outlined in a previous document (Ref. 12). Composite oxide films from the system of titanates, niobates, zirconates, and tantalates were chosen for investigation (Ref. 13). Special emphasis was placed on the titanates.

The selection of an anodizing bath for Ti and an examination of the film formation parameters were chosen for immediate attention. The effect of second component additives to the bath with respect to film formation and compatibility with the electrolyte could be examined at an early stage. Because of the relatively well-known high dielectric qualities of the family of alkaline earth titanate ceramics, the development of methods for the incorporation of alkaline earth oxides into the anodized film was given a high priority.

It was expected that composite films would require a heat treatment to achieve maximum properties. The results of Herczog (Ref. 11), in which BaTiO_3 content and particle size in a feldspar matrix were found to be controlling factors, indicate that a treatment to promote grain size growth would be necessary. The films can be treated in various manners dependent on the limits of time, temperature, and environment that the particular anodized structures can withstand.

Initial evaluation of apparently mechanically sound films was in terms of capacity and electrical loss values as measured by the use of counter electrodes on the film surface. Different types of counter electrodes (liquid, solid) and their methods of application (painting, vacuum deposition, etc.) give different levels of response on a given surface. The responses of a selected list of counter electrodes on the types of film surfaces produced were evaluated.

The results of Sibert (Ref. 14) on the anodization of Ti surfaces indicated that acid-phosphate-based baths, and in particular aqueous solutions of ethyl acid phosphate, possess superior anodic film-forming characteristics. Maxwell (Ref. 3) has found that an effective high dielectric ceramic can be produced by small additions of Sb_2O_3 to fired TiO_2 . The anodization of Ti in an ethyl acid phosphate bath with and without Sb_2O_3 appeared to be a logical point for initiation of the study.

A description of the experiments performed and the results have been organized under three general classifications based on a general type of approach. These are (1) electrophoretic deposition of particulate material, (2) anodic formation of high dielectric materials from a soluble component of the bath, and (3) the addition of small quantities of metallic or submetallic oxides either by occlusion of anionic material from the bath or by the use of alloys.

3.2 CELL DESIGN

A simple cell design was chosen. The anodizing bath was contained in a 250-ml Griffin beaker filled to near the top. A cylinder of Ti metal foil 3-in. high and 2-1/2 in. in diameter served as the cathode. The Ti metal to be anodized was cut from sheet (Titanium Co. of America, No. 55A or 75A) into strips 3-in. long and from 5/16- to 1/2-in. wide. A stop-off jig and anode support was provided by sandwiching 1-3/4 in. of the strip length between two sheets of silicone rubber backed by stiff plastic and held tight with a c-clamp. The jig was immersed approximately 1/4 in. into the surface of the bath with the longer section of exposed Ti strip extending 1 in. down the axis of the cell. The short length of the strip extending above the jig served as the anodic connection to the power supply. The bath was stirred with a magnetic stirring bar. Power was supplied to the cell by DC voltage supplies which could be both current and voltage regulated.

3.3 COUNTER ELECTRODES AND CAPACITY MEASUREMENT

The type and preparation of the counter electrodes used in measuring the capacity and losses of these films influence the readings observed. These differences in measurement arise primarily from differences in the wetting of the surface and the ability of the counter electrode to penetrate pores and microcracks in the coating. As part of the initial study, a comparison of various electrode systems was made (Ref. 15). An alternate silver paint procedure has been used most recently in addition to the silver paint tested earlier.

The counter electrodes include vapor deposited chromium; liquid mercury; a silver paint from Wornow Process Co., ink no. 140-15-u; a silver paint, DuPont No. 6730 on top of Aquadag No. 194; and finally an aqueous LiCl solution.

Some typical comparisons of observed capacities are shown in Table 3-1.

Table 3-1
COMPARISON OF CAPACITIES MEASURED WITH
VARIOUS COUNTER ELECTRODES

Substrate	Type	Bath Used	Forming Voltage	Film Firing	Capacity nF/cm ²	Loss (D)
Ti55A	Aqueous LiCl	Ethyl H ₂ PO ₄	220	No	33	0.12
Ti55A	Chromium	Ethyl H ₂ PO ₄	215	No	17	.043
Ti55A	Mercury	Ethyl H ₂ PO ₄	215	No	2.4	.025
Ti55A	Ag Paint (Wornow)	Ethyl H ₂ PO ₄	220	Yes 800° C	4.9	.035
Ti55A	Ag Paint (DuPont)	Acid (Ence)(a)	150	No	8.4	.046
Ti55A	Mercury	Acid (Ence)(a)	150	No	3.8	.25

(a) Ence's acid bath consists of 5cc 85% H₃PO₄, 5 grams oxalic acid, 5 grams citric acid, 10 cc of lactic acid, 60 cc of ethyl alcohol, and 35 cc H₂O (Ref. 16).

The high capacity using the chromium and aqueous LiCl are attributed to better contact in the pores and microcracks over the apparent electrode area. On the other hand, the high surface tension of mercury undoubtedly prevents it from entering these pores and cracks, and the capacities observed are somewhat low. The silver paint systems appear to give intermediate values indicating that better wetting is obtained than with the mercury. At the same time, no great penetration of the pores or cracks takes place to produce a very small effective thickness and larger than measured area.

A majority of the capacity measurements presented in this report have been made using either the mercury or silver paint counter electrode.

3.4 ELECTROPHORETIC TECHNIQUES

3.4.1 Deposition of Sb_2O_3 on Ti From an Ethyl Acid Phosphate Bath

Two grams of reagent grade Sb_2O_3 was added to a 250 ml ethyl H_2PO_4 bath and dispersed by stirring. After several hours a suspension of fine particles was obtained. Titanium strips were anodized in this bath shortly after the addition and again when the suspension had been obtained. The resultant films appeared identical to those prepared in plain ethyl H_2PO_4 baths. The capacity and losses measured on films formed in this bath are compared in Table 3-2 with samples formed in baths containing no Sb_2O_3 . There is no evidence of any improvement of the dielectric strengths of the film. It should be noted that alternate firing techniques might improve the dielectric strengths if there is an appreciable Sb_2O_3 content in the film.

3.4.2 Electrophoretic Deposition of CaO on Ti

Reagent grade CaO slurried in isopropanol gave an electrophoretic deposition Ti strips, pre-etched in HNO_3 -HF, when the strips were made 260 to 400 volts negative. The same cell geometry as used for the anodizations was employed. No attempt was made at this time to classify the particle size. The deposits were thick and non-uniform, and coverage was not complete. The deposits adhered to the strips on heating to 800°C followed by rapid cooling.

Table 3-2

CAPACITY AND LOSS VALUES MEASURED WITH SILVER PAINT ELECTRODES
ON Ti STRIPS ANODIZED IN AN ETHYL H_2PO_4 BATH AND FIRED AT 800°C

Strip No.	Sb_2O_3 Slurry Concentration	Ag Paint Baking Time (hr)	Maximum Voltage	Current Density (ma/cm ²)	Capacity (nF/cm ²)	Loss (D)
7A	None	1	220	29	4.9	0.035
7C	Thin	1	220	29	4.2	.028
7F	Thin	1/2	220	29	4.9	.043
7H	Heavy	1/2	220	29	4.1	.043
7J	Heavy	1/2	220	29	3.9	.044
77A	None	17	220	29	5.8	.045
7C	Thin	17	220	29	4.9	.048
7F	Thin	250	220	29	7.2	.029
7H	heavy	250	220	29	6.8	.040
7J	Heavy	250	220	29	6.7	.032
11D	Heavy	15	200	14	5.5	.050
11C	Heavy	15	250	17	4.3	.055
11A	Heavy	15	280	17	4.8	.050
11B	Heavy	15	330	19	5.0	.050

The CaO deposit dissolved rapidly in the strongly acid ethyl H_2PO_4 bath even after heat treating. Anodized films on the previously CaO -coated strips exhibited darker and lighter areas. The latter were caused by particles (presumably CaO) imbedded in the film.

The capacity measurements of these anodized coatings were in the same range as those listed in Table 3-2.

3.4.3 Electrophoretic Deposition of BaTiO_3 on Ti

Electrophoretic deposits of BaTiO_3 on Ti have been made using pyridine and pyridine- H_2O systems in which BaTiO_3 was suspended. In addition, some experiments were performed in which the BaTiO_3 coatings were fired at various temperatures and in various atmospheres.

A suspension of BaTiO_3 particles in pyridine produced very thick (on the order of mils) electrophoretic deposits on Ti strips held 250 volts negative. Excellent coverage was obtained in 25 sec. The BaTiO_3 deposit did not appear to dissolve in the ethyl H_2PO_4 bath, but a good deal of it was dislodged on anodization. Films, anodized over the BaTiO_3 deposit, contained particles of imbedded BaTiO_3 . The capacity of these films is shown in Table 3-3.

Table 3-3

CAPACITY AND LOSS VALUES MEASURED WITH SILVER PAINT ELECTRODES (BAKED 60 hr) ON Ti STRIPS, PARTLY COVERED WITH ELECTROPHORETICALLY DEPOSITED BaTiO_3 , ANODIZED AT 250 VOLTS IN THE ETHYL H_2PO_4 BATH AND FIRED AT 800°C

Strip No.	Measured Over BaTiO_3 Precoat Area	Current Density (ma/cm^2)	Capacity (nF/cm^2)	Loss (D)
26Aa	No	18	6.7	0.033
26Ab	No	18	6.0	.035
26Ac	Yes	18	7.3	.030
26Ad	Yes	18	6.8	.031
26Ba	No	3	5.7	.033
26Bb	Yes	3	5.7	.033
26Bc	Yes	3	6.0	.032

In another experiment the starting bath was a suspension of BaTiO_3 particles in pyridine. The cell was similar to that used in other anodizations except that the cathode was reduced to fit in a 100-ml beaker. The anodization voltage was 400 volts in all cases. The current densities were low and achieved only $3 \text{ ma}/\text{cm}^2$ after a large amount of H_2O was added to the bath. No evidence for the incorporation of particles into the films was found. The films ranged from a thin transparent type formed at low water content to a thick white deposit in the form of small dots at higher water concentrations. The capacity and losses of these films are shown in Table 3-4.

Table 3-4
Ti ANODIZED IN PYRIDINE - H₂O - BaTiO₃ BATHS AT 400 VOLTS

Strip No.	Water Added	Forming Time (min)	Capacity nF/cm ² (Hg Electrodes)	Loss (D)
55A	None	15	200	0.27
55B	Slight	5	6	.17
55C	Large	15	0.6	.10

Neither of these approaches provide the required capacity per unit area. However, data concerning the thickness of these films were not obtained, so an estimate of the dielectric constant is not available. If these films were of sufficient thickness, then the capacities measured could indicate some improvement in dielectric constant.

One final series of experiments was made in which 1 gram of BaTiO₃ powder was ground briefly with a small amount of pyridine in a mortar. The slurry was added to a 100-ml-size cell and diluted to 75 ml with pyridine. Deposition was carried out with the axial Ti strip at 195 volts negative. Excellent coverage of BaTiO₃ was obtained in 30 to 60 sec.

Capacity and loss values following various heat treatments are presented in Table 3-5. No sintering was observed for the BaTiO₃ deposits heated to 1000° C in air or to 1080° C in vacuum. The deposits still adhered to the Ti substrate, but could be wiped off with a towel. After firing at 1250° C in vacuum, the BaTiO₃ had a sintered, metallic-gray appearance. Deposits fired at both temperatures in a vacuum were highly conducting whereas the air-fired deposits were resistive. The conductive deposits could be made resistive by heating in air. (See Table 3-6.)

Table 3-5
HEAT TREATMENT OF BaTiO₃ DEPOSITS

Film Type	Heat Treatment	Capacity nF/cm ² (Hg Electrodes)	Loss (D)
Bare Ti	800° C, Air, 1 hr	28.0	0.14
Thick BaTiO ₃ Deposit on Ti	Dried RT	0.3	.15
	800° C, Air, 1 hr	1.0	.5
	1000° C, Air, 1/2 hr	0.6	.3
	1080° C, Vacuum, 1/3 hr	100×10^3	40
	1250° C, Vacuum, 1/2 hr	60×10^3	33
Film Grown Under BaTiO ₃	800° C, Air, 1 hr	40.0	0.3
	1000° C, Air, 1/2 hr ^(a)	3.0	.2
Ti - BaTiO ₃ Deposit, Anodized in Ethyl H ₂ PO ₄	1000° C, Air, 1/2 hr	3.0 to 24	.2
Film Grown Under Combined Deposit and Anodization	1000° C, Air, 1/2 hr	26×10^3	30

(a) A thick white film.

Table 3-6
HEAT TREATMENT OF CONDUCTIVE COATING

Original Heat Treatment (° C)	After Heating to Red Heat in Flame		After Firing 1/2 hr at 800° C in Air	
	Capacity nF/cm ² (Hg electrodes)	Loss (D)	Capacity (nF/cm ²)	Loss (D)
1180	100	0.07	26×10^{-3}	0.15
1250	400	.6	2.4	.16

3.4.4 Discussion

These preliminary experiments are somewhat ambiguous. The BaTiO_3 used in the electrophoretic deposition has a typical dielectric constant and a capacity of about 10 times the capacitance which was observed and which would be expected for thick BaTiO_3 deposits [assuming them to be about 1 mil (25.4μ) in thickness]. A recheck of the BaTiO_3 was made by painting a slurry of the dielectric in Kasil 88 on a strip of polished titanium and aluminum. The dielectric constants of these paints on both substrates were greater than 10^3 . The anomalous results of the electrophoretic coatings may be due either to the counter electrode used in the measurement, or the coatings may be much thicker than has been assumed. If the electrophoretic coatings are 1-mm thick, then the a RT-dried BaTiO_3 coating would have a dielectric constant of about 300. The results, and the unresolved questions concerning them, suggest that additional data be obtained to determine the actual dielectric constant of such coatings.

3.5 ANODIC FORMATION OF TITANATES, ZIRCONATES, AND NIOBATES

3.5.1 Introduction

A second approach to the formation of a high dielectric film consists of anodizing the substrate metal and depositing a second oxide material either during anodization or by impregnating the porous anodic coating in a separate step. The experiments performed have been directed toward preparing films containing barium titanate, lead titanate, lead zirconate, and potassium niobate. The data presented are primarily in terms of capacity measurements. Some qualitative analyses of the films are also presented. The experimental results are grouped according to substrate used and are in the order of titanium, zirconium, and niobium.

3.5.2 Films Formed on Ti in Barium-Containing Baths

The simple ethyl H_2PO_4 and the ethyl H_2PO_4 -barium phosphate baths have been described previously (Ref. 15). Films produced in these baths under high, limited current, anodizing conditions are listed in Table 3-7. In the simple bath, arcing was

observed only in the gas phase (produced by a gas bubble collected under the jig). In the barium-containing bath, arcing took place randomly over the strip surface producing small areas of white debris. Forming times were made short to preserve enough unsparked area to allow placement of the counter electrode. The films were measured after drying at 110° C and then after firing at 800° C in air. The white arc product areas had much lower capacities than the unsparked gray film areas listed in the table.

Titanium strips were also anodized in solutions containing 3 grams $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ or 5 grams $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot n\text{H}_2\text{O}$. Capacity and loss values after drying at 110° C and after firing at 800° C are listed in Table 3-8. Arcing took place at 195 volts in the hydroxide bath. The acetate bath-formed films, after firing at 800° C, exhibited lower capacities and higher losses than before firing. The values changed rapidly during measurement, indicating atmospheric sensitivity.

Ti strips were also anodized in a bath of fused $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ contained in a nickel crucible which also served as the cathode. The barium hydroxide was maintained somewhat above its melting point of 78° C. No stop-off was used. A constant, limited current was employed. At 60 ma/cm² a voltage of 30 was reached. The film has a capacity of 0.6 nF/cm² at $\eta_s = 0.03$. At 160 ma/cm² a voltage of 50 was reached with arcing. The capacity of the resulting film was about 0.08 nF/cm² on all areas.

3.5.3 Additions to Films by Dipping

Strips of Ti having freshly dried anodized films were dipped into a solution of barium acetate and dried. The procedure was repeated until the weight gain of the strip indicated that sufficient barium values has been added to very roughly approximate the number of moles of Ti present in the film. The weight gain was not adequate until a thick deposit was laid down on the surface of the film.

The films dried at 110° C do not appear sufficiently porous to allow the incorporation of significant quantities of liquid by dipping. Increased amounts might be added by dipping under vacuum, especially if the films were rendered more porous by firing or high current preparation.

Table 3-7

CAPACITY AND LOSS VALUES FOR Ti STRIPS ANODIZED AT HIGH CURRENTS
IN SIMPLE ETHYL H_2PO_4 AND ETHYL H_2PO_4 -BARIUM PHOSPHATE BATHS

Strip No.	Bath	Forming Time (min)	Max. Voltage Attained	Current Density (ma/cm ²)	After Drying		After Firing	
					Capacity (nF/cm ²)	Loss (D _S)	Capacity (nF/cm ²)	Loss (D _S)
42M	Simple	2	—	190	13	0.55	130	0.27
42N	Simple	4 ^(a)	380	190	7.2	.42	8.6	.67
45R	With Ba	1/2	130	210	70	.75	20 ^(b)	1.3
45S	With Ba	1/4	130	240	180	.53	80	0.7

(a) Bath boils after 4 min.

(b) Parallel equivalent circuit measurement.

Table 3-8

CAPACITY AND LOSS VALUES FOR Ti ANODIZED IN BARIUM HYDROXIDE
AND BARIUM ACETATE BATHS

Strip No.	Voltage Limit	Forming Time (min)	Current Limit (ma/cm ²)	Final Current (ma/cm ²)	Bath	After Drying		After Firing	
						Capacity (nF/cm ²)	Loss (D _S)	Capacity (nF/cm ²)	Loss (D _S)
21A	50	30	20	9	Hydroxide	300	0.5	240	0.4
21B	100	30	160	30	Hydroxide	320 ^(a)	.4	28	.08
21C	150	30	160	160	Hydroxide	Variable		30 ^(b)	.7
21D	195	185	160	4	Hydroxide	0.2	Low	—	—
32A	100	35	40	2	Acetate	2.0	0.25	—	—
32B	280	45	160	10	Acetate	38	.09	—	—

(a) Parallel equivalent circuit measurement.

(b) Value listed is for arc debris areas. Nonsparked areas had low C and high D.

3.5.4 Reaction of Anodized Ti Films With Barium Hydroxide

Opaque gray films were formed on Ti strips by anodizing in an ethyl H_2PO_4 at 20 ma/cm^2 to 225 volts. After drying, parts of the strips were dipped for a few seconds into fused $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ (melting point about 78°C) to form a thick coating. The coated strips were heated in air briefly to 550°C and then held for 30 min at 400°C . The resultant thick, flaky coating was washed off with water, the strips dried at 110°C , and the capacity measured with a mercury counter electrode. The dipped portions of the film exhibited a capacity of from 0.4 to 0.8 nF/cm^2 while the undipped portions were higher at 4 to 10 nF/cm^2 . The loss values were low - less than one percent. Treating the reacted strips with the strongly acid ethyl H_2PO_4 anodizing bath (to remove traces of barium hydroxide) and then rinsing and drying raised the capacities of both sections but also increased the loss:

Undipped - 15 nF/cm^2 at $D = 0.25$

Dipped - 1.3 nF/cm^2 at $D = 0.1$

Refiring at 850°C for 1 hr in air raised the values for the dipped film area to 3 nF/cm^2 at $D = 0.2$ and simultaneously reduced the capacity of the undipped film area.

Thicker, more porous anodic films were formed on Ti strips by anodizing in the ethyl H_2PO_4 bath for 1-1/2 min at 140 ma/cm^2 to approximately 300 volts. These films were allowed to stand in the fused $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ for about 1 min. The strips with their thick dip-coats were then fired in air for 3-1/2 hr at 400°C followed by 1/2 hr at 850°C . After removing the unreacted excess by dissolving in ethyl H_2PO_4 and rinsing and drying, the portions of the films exposed to barium hydroxide contained three distinct types of regions: relatively smooth black film with an average capacity of 1.2 nF/cm^2 at $D = 0.25$; cracked and peeling white product area with an average capacity of 0.40 nF/cm^2 at $D = 0.5$; and a very thin, yellow film area (where the thick films had fallen off) exhibiting a widely variable high capacity averaging about 6000 nF/cm^2 at $D_p = 2.5$. The film areas not exposed to barium hydroxide gave an average capacity of 1.0 nF at $D = 0.1$.

In an alternate procedure the anodized Ti strips were dipped into fused Ba(OH)_2 which has a melting point of about 408°C . In this case the reaction proceeded directly to give a rough and porous white product which did not adhere to the Ti substrate. Capacity measurements could not be made.

3.5.5 Films Formed on Ti in Baths Containing Complexed Barium

Opaque white to yellow coatings are formed on titanium when it is anodized under breakdown potential conditions. Two types of baths have been used. The bath compositions are shown in Table 3-9 along with the semiquantitative spectrographic analysis of the films. Under the conditions employed, the higher pH baths produced coatings with more occluded barium than the acid pH baths.

Table 3-9
ANALYSIS OF FILMS FORMED IN Ba-EDTA BATHS

Bath pH	Bath Composition	Semiquantitative Analysis of Film ^(a)
5	2.5 grams KOH 15 grams EDTA 11 grams $\text{Ba(C}_2\text{H}_3\text{O}_2)_2$ 500 ml H_2O	Major: Ti ^(b) Minor: Ba ^(c)
9	2.5 grams H_3BO_3 10 grams KOH 15 grams EDTA 11 grams $\text{Ba(C}_2\text{H}_3\text{O}_2)_2$ 50 ml H_2O	Major: Ba, Ti Minor: B

(a) Stripped in bromine methanol from substrate.

(b) Major = 10-90 percent by weight.

(c) Minor = 1-10 percent by weight.

Interpretation of the capacity values is complicated by the variation in thickness of the coatings produced and by another factor heretofore ignored. This factor concerns the crystallinity of the material and the probability that for coatings of this type, the material is not entirely barium titanate. The work of Müller, Nicholson, and Francombe (Ref. 17) shows that crystallinity must be present before appreciable increases in dielectric strength are observed. Any of the films prepared by methods used so far might contain amorphous material capable of developing a high dielectric if sufficient crystallinity can be induced.

In addition, the work of Herczog (Ref. 11) has shown that in a composite material consisting of two different materials with different dielectric constants, the dielectric constant of the composite increased with the concentration of the high dielectric material. In addition, the measured dielectric constant was very dependent upon the grain size of the high dielectric material.

The results of these investigations are encouraging and together with the data showing that barium can be deposited in an anodic film on titanium, the preparation of a high dielectric coating by electrochemical methods should be possible provided the right processing conditions are used.

3.5.6 Films Formed on Ti in KOH Plumbite Baths

Thick black films are formed on titanium in baths containing 3 grams KOH and 1 gram $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ in 250 ml under conditions listed in Table 3-10. When bath concentrations are increased to 20 grams KOH and 5 grams $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$, more variable films were produced with capacities ranging from 500 to 35,000 nF per strip at loss values of about 2 — this with forming currents limited to 10 or 35 ma/cm². When the forming current was not limited, the thick films were loose and powdery. Here, as in the case of the thick black films on Nb substrates, the capacities were roughly proportional to the total anodized area of the strips.

Table 3-10

CAPACITY AND LOSS VALUES FOR THICK BLACK FILMS FORMED ON
Ti STRIPS IN A 3/1 KOH-PLUMBITE BATH AT 20 VOLTS,
CURRENT LIMITED TO 35 ma/cm

Strip No.	Strip Pretreatment	Forming Time (min)	Final Current (ma/cm ²)	Capacity per Strip (nF)	Loss (Dp)
13E	Acetone	2	10	1500	0.61
13B	HF-HNO ₃	15	11	1000	1.0
13A	H ₂ SO ₄ -Chromate	15	8	850	0.47
13D	Acetone	25	6	940	.30

By employing short anodizing times, more dilute baths, or higher forming potentials, films could be produced on Ti in KOH-plumbite baths that were thin and multicolored and did not exhibit a total anodized area-capacity dependence. They were usually produced with a thin deposit of gold or brown colored dust on the surface. Up to about 40 volts, these films exhibited high losses (D values from 1 to 2) and capacities ranging from 400 to 10,000 nF/cm². At higher forming potentials, films with losses less than 1 were obtained. Table 3-11 lists only those films having capacities of 200 nF/cm² or higher and losses of 1 or lower. Measurements made using aqueous LiCl counter electrodes (after measuring a given strip using mercury) yielded higher capacities and the same or slightly lower losses. Firing at 800° C in air drastically reduced the capacity values of these anodized films.

3.5.7 Films Formed on Ti in Other Lead-Containing Baths

The results with simple lead acetate baths and with the lead complexed by EDTA are presented in Table 3-12. The bath concentration numerator refers to the grams of Pb(C₂H₃O₂)·3H₂O and the denominator to the grams of Na₂EDTA·2H₂O.

Table 3-11

CAPACITY AND LOSS VALUES FOR THIN FILMS FORMED ON Ti STRIPS IN KOH-PLUMBITE BATHS

Strip No.	Pretreatment	Forming Voltage	Forming Time (min)	Limiting Current (ma/cm ²)	Final Current (ma/cm ²)	Bath Concentration	Capacity (nF/cm ²)	Loss (Dp)
Forming Voltage Reached Limit								
13G	Acetone	50	1	35	10	3/1	400 ^(a, b)	0.19
64A	Acetone	120	30	35	30	2/0.1	280	.50
Forming Voltage Did Not Reach Limit								
18A	Acetone	40	20	35	35	12/4	1400	.79
56D	Acetone	45	5	10	10	1/0.05	800	1.0
61B	Acetone	45	30	10	10	0.3/0.1	640	0.75
56E	Acetone	50	3	10	10	1/0.05	600 ^(b)	.55
56G	Acetone	55	2	10	10	1/0.05	200	.30
61A	25% HF	55	30	10	10	0.3/0.1	280	.45
13I	Acetone	70	2	35	35	3/1	200 ^(b)	.30

(a) A series equivalent circuit measurement.

(b) Brown dust wiped off surface prior to measurement.

Table 3 12

Ti ANODIZED IN LEAD ACETATE BATHS WITH AND WITHOUT EDTA ADDED

Strip No.	Voltage Limit	Forming Time (min)	Limiting Current (ma/cm ²)	Final Current (ma/cm ²)	Bath Concentration	Capacity (nF/cm ²)	Loss (D _s)
68B	150	15	6	2	1/0	160 ^(a)	0.14
68A	150	3	25	4	1/0	140 ^(a)	.22
36B	100	22	160	3	5/0	60	.26
72A	150	10	10	4	1/0.3	120	.055
72B	150	15	35	15	1/0.3	150	.090
72C	100	30	10	2	1/0.3	180	.090
72D	50	40	10	10	1/0.3	300	.13

(a) Parallel equivalent circuit measurements.

Other baths were prepared by dissolving $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2) \cdot 3\text{H}_2\text{O}$ in 100 ml of 30% K_2SiO_3 and diluting to 250 ml. Using 0.1 gram lead acetate, a forming potential of 125 volts, and current densities of 10 to 150 ma/cm^2 , films with capacities of about 40 nF/cm^2 at $D_p = 0.15$ were produced. Scintillations were observed at the highest current densities and the film values were not internally consistent. When the lead acetate content was increased to 1.0 gram, the forming potential, could not be raised past about 70 volts at current densities to 30 ma/cm^2 .

One Ti strip was anodized in a bath prepared from 5 grams $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ and 5 grams $\text{ZrO}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$. After 6 min at high current, a potential of only 25 volts was attained and arcing set in. The resulting film had no measurable capacity.

3.5.8 Films Formed on Zr in Lead-Containing Baths

Films were grown in a simple bath made from 5 grams $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$. The capacity and loss values are given in Table 3-13. The films were an opaque gray when formed at 100 volts or greater.

Table 3-13
CAPACITY AND LOSS VALUES FOR FILMS FORMED
ON HF-HNO_3 -ETCHED Zr STRIPS IN A LEAD ACETATE BATH

Strip No.	Forming Voltage	Forming Time (min)	Limiting Current (ma/cm^2)	Final Current (ma/cm^2)	Capacity (nF/cm^2)	Loss (D_s)
39B	100	60	40	1	120	0.49
42C	100	2	120	6	48	.14
36A	100	12	40	7	40	.08
36E	100	1	40	3	20	.006
42A	20	30	60	1	40	.032
39A	150	12	45	3	20 ^(a)	.16
42E	200	1	80	80	20	.16
42G	250	30	80	3	10	.07
42F	300	3	140	100	8	.07

(a) A parallel equivalent circuit measurement.

Efforts to grow the high capacity per strip, thick, black films (as are obtained on Nb and Zr substrates in a KOH-plumbite bath at 20 volts) were not successful. A uniform black film was obtained on Zr in a KOH-plumbite bath at 50 volts but it had no measurable capacity. Scintillations were observed in a 9/3 KOH-plumbite bath at 70 volts and arcing at 130 volts. Increasing the KOH concentration decreased the voltage at which the scintillations first appeared. Capacities of the spark-grown films were low; the highest observed value was 0.6 nF/cm^2 .

A thick white film was grown on Zr at 300 volts in a bath containing 5 grams $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ and 5 grams $\text{ZrO}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$. After 13 min the current was still passing at the rate of 120 ma/cm^2 . The capacity of this film was 0.2 nF/cm^2 .

Zirconium strips having gray films formed in a lead acetate bath were heated at 1150°C for 15 min in vacuum. The films disappeared leaving a bright, coarse-grained metallic surface. A zirconium strip having a very thick white film formed in a zirconyl nitrate-lead acetate bath was heated at 1250°C for 30 min. A gray, low resistance film remained; however, the substrate metal was brittle and shattered into small fragments.

3.5.9 Discussion of Results Using Ti and Zr in Lead-Containing Baths

Anodizations in lead-containing baths generally result in the formation of a conductive lead oxide coating or in thin coatings. The results with titanium anodes in a bath containing the lead complexed with EDTA show interesting possibilities because the films are not conductive. Similar baths were not tried with zirconium anodes but should be investigated.

3.5.10 Films Formed on Nb in an Ethyl Acid Phosphate Bath

The bath contained 50 ml ethyl H_2PO_4 and 200 ml H_2O . Anodizations were carried out for 15 to 30 min, at which time, the current dropped off quickly (strips 68B and 73C are exceptions). The films were dried at 110° to 200°C . The results are listed in Table 3-14.

Table 3-14

Nb STRIPS ANODIZED IN AN ETHYL ACID PHOSPHATE BATH

Strip No.	Forming Voltage	Current Density (ma/cm ²)	Capacity (nF/cm ²)	Loss (D)	Remarks
68B	150	20	60	0.04	(a)
68C	195	25	1.0	.01	(b)
68D	195	30	1.0	.003	(b)
73B	202	35	1.4	.007	(b)
73C	235	55	2.0	.013	(c)

(a) Current drops very quickly. Thin, transparent film.

(b) Opaque, rose-gray film. Incomplete coverage.

(c) Current drops only by 1/2 after 30 min. Gray, opaque film. Excellent coverage.

3.5.11 Films Formed on Nb in Cadmium-Containing Baths

The simple baths were prepared by dissolving 5 or 20 grams of CdSO₄. Alternately, 1 gram KOH or 6.5 grams KCN were also added.

The results are listed in Table 3-15. When silver paint counter electrodes were employed, the capacities were lower and the losses higher. The simple baths produced thin, transparent, rose-colored films at 100 volts. At 200 volts the film was gray. Scintillations were observed when anodizing to 300 volts in the KOH-containing bath. The film on strip 26B was a thick ceramic white. The cyanide-containing bath produced gray films with scintillations at the higher current densities.

3.5.12 Films Formed on Nb in KOH-Plumbite Baths

The baths were prepared by adding lead acetate trihydrate to a solution of potassium hydroxide. The resultant solutions contained excess potassium hydroxide, potassium acetate, and a soluble lead hydroxide (the latter usually referred to as plumbite).

Table 3-15
CAPACITY AND LOSS VALUES FOR FILMS FORMED ON
Nb STRIPS IN SIMPLE CADMIUM SULFATE BATHS

Strip No.	Forming Voltage	Forming Time (min)	Limiting Current (ma/cm ²)	Final Current (ma/cm ²)	Bath Concentration	Capacity (nF/cm ²)	Loss (D _s)
34C	50	2	160	0.2	20/0	180	0.038
34B	100	30	160	2	20/0	100	.022
34A	100	30	160	0.1	20/0	110	.04
30A	100	30	20	.1	5/0	120	.012
26A ^(a)	190	10	160	1	5/0	70	.006
30B	200	30	160	1	5/0	50	.008
With 1 gram KOH Added to Bath							
26C	100	30	160	0.2	5/1	120	.011
26B ^(a)	300	Short	160	120	5/1	0.6 to 8.0	0.1 to 0.6
With 6.5 grams KCN Added to Bath							
24A	195	—	35	3	5/6.5	10	.025
24B	200	—	160	60	5/6.5	8	.03
24C	200	—	160	60	5/6.5	12	.5

(a) Nb Strip was preplated with a film of Cd metal.

Using a bath prepared from 20 grams KOH and 5 grams $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$, untreated Ti strips, current limited up to 40 ma/cm², and limiting potentials of 15 to 20 volts, a two-stage film growth was observed. A thin, transparent, blue film formed rapidly and the current dropped to a variable fraction of the preset limit. Black dots then appeared, scattered over the film surface. On prolonged anodization (several hours) the black dots coalesced giving the appearance of a thick, dendritic, black film covering a major portion of the initially formed thin blue film. Capacity and loss values ranging from 2 μF at $D_s = 0.25$ to 7 μF at $D_s = 1.0$ were obtained for strips having an anodized area of 2.5 cm² per side. For any given strip the measured capacities were relatively insensitive to the area of the mercury or silver paint counter electrodes employed.

Thick black films were grown by anodizing for 1 hr (under the conditions described above) and then the films were stripped off the Nb substrates by reanodizing in a 25 vol % ethyl H_2PO_4 bath. A spectrographic analysis yielded a niobium content of 0.15 wt % in the stripped film.

Various Nb substrate pretreatments and anodization parameters were investigated to improve the quality of the KOH-plumbite bath films and to prepare them faster. Soaking the strips in H_2SO_4 -chromate (glass cleaning solution) prior to anodization, and then anodizing without current limitation gave the fastest growing and most uniform black films. Under these conditions, an initial current surge of about 200 ma/cm^2 was observed. A silver paint counter electrode drying time of about 40 hr at 110°C appeared to give minimum losses. (Prefiring the Nb strips at 400°C , precoating them with an electrolytic lead film, preanodizing in a plain KOH bath, and reducing the electrode spacing of the anodization cell did not appear to be of any benefit.) The optimum forming potential was 15 to 20 volts. Raising the voltage much above 20 led to scintillations and apparently a different type of film growth mechanism. In those cases, the usual black films were not obtained and the capacities were reduced drastically.

Examples of capacity and loss data for strips exhibiting uniform black films are listed in Table 3-16. The capacities were still roughly proportional to the film area (5 cm^2) and independent of the area of the counter electrode. Several of the films were given further electrical tests. Strip 104C exhibited a resistance of 12 megohms at 1.5 volts DC and 1 megohm at 2.0 volts DC. For strip 1C, the DC resistance was 20 megohms at 2 volts and 1 megohm at 8 volts. Typical curve tracer observations are given in Table 3-17. The testing potentials were raised rapidly, taking only a few minutes to reach the breakdown point. The DC resistance and breakdown potentials were measured using silver paint counter electrodes with the counter electrodes always at negative (or ground) potential. Reversing the current flow resulted in breakdown at only a few volts.

Table 3-16

CAPACITY AND LOSS VALUES FOR THICK BLACK FILMS FORMED
ON H_2SO_4 -CHROMATE-SOAKED Nb STRIPS IN KOH-PLUMBITE
BATHS AT 20 VOLTS(a)

Strip No.	Bath Concentration $\frac{\text{g KOH}}{\text{g Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}}$	Forming Time (min)	Capacity per Strip (nF)	Loss (D_s)
104C ^(b)	12/4	60	360	0.15
107A	15/4	60	1100	.35
1B	20/4	30	660	.13
1C	20/4	30	650	.15
2C	12/4	22	630	.10
4A	20/4	90	370	.30
4B	20/4	120	440	.40
IDA ^(c)	3/1	15	1100 ^(c)	.30

(a) Current unlimited; silver paint counter electrode drying
time approximately 20 hr.

(b) Nb strip soaked in 8N HNO_3 .

(c) Mercury counter electrode used.

Table 3-17

TYPICAL CURVE TRACER OBSERVATIONS

Strip No.	Current at 20 Volts (ma)	Breakdown Potential (volts)
104C	2.0	27
107A	3.5	28
1B	3.5	25

3.5.13 Reaction of Anodized Nb Films With Potassium Hydroxide

Niobium strips containing opaque films grown in the ethyl H_2PO_4 bath were dipped briefly into fused KOH. (Too long an immersion time resulted in complete dissolution of the film and attack on the metal substrate.) After rinsing off the excess KOH with water, a change in film color from gray or rose-gray to white was observed. After drying at 110°C , capacities of approximately $60\ \mu\text{f}/\text{cm}^2$ at $D_p = 4$ were observed. After a few minutes out of the oven the capacity fell off and the loss increased. After reheating to 400°C , the capacity was partially restored to about $4\ \mu\text{f}/\text{cm}^2$ but the loss was 33. Reanodizing the dipped films in the ethyl H_2PO_4 resulted in values not as good as ordinary anodized films.

Niobium strips with the gray films grown in the cadmium-containing baths were also dipped in fused KOH to produce a white product. Using the No. 24 strip series (subsection 3.5.11), reacted films with an average capacity of $0.8\ \text{nF}/\text{cm}^2$ at $D_s = 0.01$ to 0.06 were produced after rinsing and drying. Dipped strip No. 26B was $18\ \text{nF}/\text{cm}^2$ at $D_s = 1.0$ after a similar treatment.

3.5.14 Discussion of Results With Niobium Anodes

The attempts to introduce potassium or cadmium into niobium anodic films were unsuccessful. In fact, baths using KCN to complex the cadmium in anionic form produced poorer films than usually encountered. Dipping the films in fused KOH generally resulted in poorer films, although the one series using the films produced in the cyanide bath containing cadmium did show some very interesting electrical properties.

3.6 FORMATION OF DOPED FILMS

3.6.1 Introduction

A third approach used to prepare anodic films possessing superior electrical characteristics is the occlusion of minor amounts of certain oxides within the film. Two

methods were selected to evaluate this approach. The first is to occlude small amounts of certain oxides from the electrolytes. The oxides of phosphorous, arsenic, lead, antimony, and boron have been prepared as the anionic portion of a complex. Samples of titanium were anodized in baths containing these complexes and the electrical characteristics measured. The second method used involves the anodization of certain alloys of titanium and niobium. This approach presumes that the alloying metals are uniformly distributed and that the solubility of these metal oxides will not be too great in the electrolyte used. The coatings produced by these approaches are quite thin. The thickness of the films can be estimated by color interference methods. The work in this area has also lead to an evaluation of substrate preparation.

A comparison of the electrical properties for films prepared in various doping electrolytes is shown in Table 3-18. These films and their formation were discussed in an earlier report (Ref. 18). The results of those experiments as shown in this table indicated that the nature of the electrolyte does affect the electrical values observed. Further experiments and studies have been conducted since that report to investigate these differences.

3.6.2 Surface Preparation

The effect of surface preparation on voltage-time curves and electrical capacity of the anodic films has been discussed previously (Ref. 18). The results of these studies showed that the surface preparation had no effect on the electrical capacitance of films formed to 100 volts in either acid or basic electrolytes. However, distinct differences in voltage-time relationships were observed. The nonlinear curves obtained probably reflect changes in efficiencies due to the presence of impurities and an oxide prior to anodization.

3.6.3 Film Thickness of Titanium-Based Films

The fundamentals of film thickness measurement by the interference color method has been previously reported (Ref. 18). The film thickness as a function of voltage is shown in Fig. 3-1. The slope of the line is equivalent to 21 A/volt.

Table 3-18

FILMS PREPARED IN DOPING ELECTROLYTES

Bath Constituents	Concentration (g/l)	Capacitance ($\mu\text{f}/\text{cm}^2$)	Loss (D)	Final Voltage	Current Density (ma/cm^2)
KOH	4	0.200	0.09	100	10
	40	.130	.30	100	10
NaOH	4.0	.074	.14	100	10
	40	.076	.23	100	10
$\text{Na}_2\text{HASO}_4 \cdot 7\text{H}_2\text{O}$	4	.340	10.	100	10
	100	.120	0.14	100	20
	200	.260	.28	80	10
$\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$	4	.001	.24	100	10
	200	.005	.82	85	150
$\text{K}_4\text{Sb}_2\text{O}_7$	4	.160	.23	100	10
$\text{Na}_2\text{HASO}_4 \cdot 7\text{H}_2\text{O}$	100	.180	.15	100	10
$\text{K}_2(\text{C}_3\text{O}_4)$	20				
$\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$	4	.169	.18	100	10
KOH	4				
H_3BO_3	0				
KOH	5				
EDTA	30	.154	.17	100	10
$\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$	22				
H_3BO_3	5				
KOH	5	.104	.16	100	10
EDTA	30				
$\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$	22				
H_3BO_3	5				
KOH	5	.120	.12	100	10
EDTA	14				
$\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$	22				
Ethyl H_2PO_4	30	.021	.038	100	12

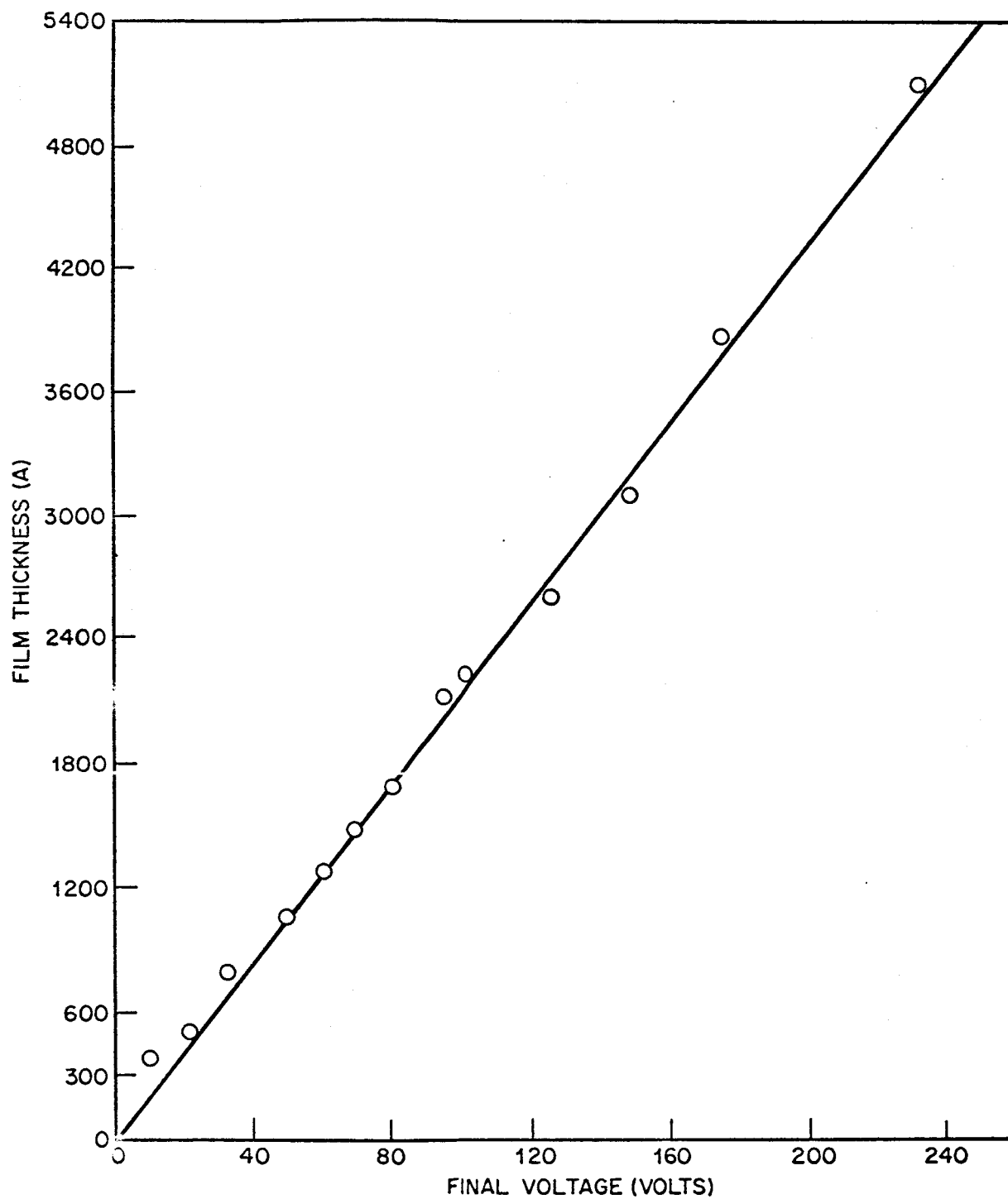


Fig. 3-1 Film Thickness as a Function of Anodizing Voltage

3.6.4 Dielectric Constants of Thin Doped Films on Titanium

The dielectric constants of films formed on three alloys of titanium in three different baths are shown in Table 3-9. All surfaces were polished in the same manner. The results show that the presence of aluminum, vanadium, or tin in the amounts listed do not increase the dielectric strength of the films formed in any of the baths. In all baths evaluated, the titanium 55A formed films with similar dielectric properties, with some indication that the properties improved with increasing acidity. The voltage-time curves were similar for all substrates and all baths. However, higher voltages were obtainable in the acid bath.

3.6.5 Dielectric Constants and Resistances of Films Formed on Ti and Ti Alloys (Using Silver Paint Counter Electrodes)

A set of samples was produced and painted with silver Aquadag counter electrodes to test the electrical resistance of the films produced and to compare capacitance measurement.

In general, the capacitance measurements were all approximately one-third the value measured with mercury counter electrodes. Thus the dielectric constants calculated from these electrodes are about one-third those shown in Table 3-19.

The resistances of these films were measured with silver paint counter electrodes. The values observed increase with the film thickness, i. e., formation voltage, and decrease rapidly in all cases as the voltage applied across the film is increased.

As might be expected from the previous results, no measurable difference was found for films formed in different baths or for films formed on different alloys.

3.6.6 Conclusions

Review of the literature, experimental work performed, and evaluation of tests made in this laboratory indicate that to have a high dielectric constant, coatings should

Table 3-19

DIELECTRIC CONSTANTS OF FILMS FORMED ON Ti AND Ti ALLOYS

Voltage	Bath								
	Ence's Acid Bath (C.D. 1 ma/cm ²)			100 grams Na ₂ HAsO ₄ (C.D. 5 ma/cm ²)			4 grams Na ₂ HAsO ₄ (C.D. 5 ma/cm ²)		
	55A	6Al-4V	6Al4Sn	55A	6Al-4V	6Al4Sn	55A	6Al4V	6Al4Sn
2.5	—	—	—	—	—	—	20	—	—
5	38-14	18	27	36	—	14	18	—	—
10	40-26	9	15	30	21	—	31	19	27
15	—	—	—	28	—	—	30	—	—
20	40	21	17	37	—	22	32	23	18
30	—	16	23	—	—	18	—	—	25
40	—	—	—	33	19	—	32	—	—
50	33	17	24	—	—	20	—	—	21
60	27	—	23	—	25	21	—	25	23
70	31	23	23	—	—	24	23 ^(a) (75 v)	—	22
80	29	23	24	27	—	23	—	—	28
90	32	23	19	—	23	23	—	—	23
100	22	21	21	24	—	21 (35)(a)	—	23	—
110	28	—	—	—	—	—	—	—	—
125	24	17	14	—	—	—	—	—	—
175	—	32	22	—	—	—	—	—	—
200	—	21	—	—	—	—	—	—	—

(a) Coating broke down.

Note: All capacitance measurements made with Hg counter electrodes.

contain crystals of about 1 μ in size. This suggests that electrophoretic techniques may be most feasible for obtaining high dielectric constant coatings.

The formation of variously doped and modified titanium oxide films has been attempted by anodic oxidation. Of the methods evaluated, one appears to be a

successful approach: the inclusion of barium from its EDTA complex during sparking conditions.

The use of arsenate, stannate, and lead-containing aqueous solutions, and of tin and vanadium alloys of titanium, resulted in anodic oxidic films having visual and electrical properties similar to titanium oxidic films.

In general, there are three methods by which anodic oxidic films grow:

- (1) The oxidic film grows at the oxide-solution interface; the metal is transported through the film.
- (2) The oxidic film grows at the metal-oxide interface; the oxygen (e. g., anion) is transported through the film.
- (3) The oxidic film grows by a combination of the above two processes.

Comparison of the above methods with the results obtained allows several postulates.

For Method (1):

- The arsenate and stannate will not be included in the film, if the TiO_2 reaction is "easier," until the film is such that the concentration of titanium on the surface will allow a second reaction. If this reaction is such that the electronic current in the film becomes predominant, then a second film is formed which contains no titanium. Conductive films of tin and lead oxide are examples of these and both have been observed experimentally.
- The vanadium and tin in the alloy are not transported into the film and thus are not included in the film.

For Method (2):

- The lattice spacing in the film and/or water content of the bath is too great to allow diffusion of the arsenate or stannate ions into the film.
- The vanadium and tin in the alloy are transported through (out of) the film as, e. g., cations.

For Method (3):

- This is a combination of the above processes and proceeds as described.

Examination of these postulates indicates that the second postulate in Method (2) is the least feasible and therefore the most probable postulates are those in Method (1).

There is a high percentage of electronic current present when titanium is oxidized anodically. Thus, if the titanium is of a concentration at the oxide-solution interface so that a second reaction is possible, the second reaction becomes immediately predominant and a second, different film (e. g. , a tin oxide) is formed.

3.6.7 Capacitances and Resistances of Films Formed on Niobium and Fansteel 80 Metal

The capacitances of films formed on niobium and Fansteel 80 in two baths are shown in Table 3-20. The results indicate no particular differences due to bath electrolyte. However, the Fansteel films appear to be somewhat superior in characteristics to the niobium films in the ethyl phosphate bath.

The resistances of Fansteel films were about ten times as great on the average at low applied potentials. However, at higher potentials the resistances were similar. It is concluded that no improvement in films is made by adding tantalum to niobium.

Table 3-20

CAPACITANCES OF FILMS FORMED ON NIOBIUM AND FANSTEEL 80 METAL

Voltage	Current Density (ma/cm ²)	Bath			
		250 ml Ethyl Hydrogen Phosphate per liter		0.2 NH ₂ SO ₄	
		Nb (μf/cm ²)	Fansteel (μf/cm ²)	Nb	Fansteel
50	8	0.083	0.034	0.071	
100	8	.053	.053	.054	0.046
150	8	.035	.051	.047 (140 volts)	.043 (180 volts)
175	8	.032	.040		
50	16			.059	.055
100	16			.054	.048
50	30			.046	.073
100	30				.062
150	30				.044
200	30				.035

Section 4

SUMMARY AND RECOMMENDATIONS

Three methods were proposed at the beginning of this study to prepare high dielectric films.

- Attempts to improve the dielectric constant by doping the film, either from the bath or by introducing the doping elements by alloying the titanium with aluminum, and/or vanadium and tin, do not result in significant improvements in the dielectric strength of the film. On the contrary, these procedures tend to cause deterioration of this property. It is not recommended that further work be done in this area.
- Attempts to produce mixed oxides by decomposition of a second oxide as part of the electrolytic conversion process has been shown to occur. Further work using this technique should include detailed study on the effect of bath composition, the amount of the second oxide phase deposited, measurement of thickness for dielectric strength determination, and the effect of post-anodization treatments on crystallinity and on the electrical properties.
- The deposition of high dielectric material such as barium titanate by electrophoretic techniques has been performed. Incorporation of such a process to provide a useful component should be further pursued. A more detailed study of the dielectric strength of such films should be carried out.

Section 5

REFERENCES

5.1 CITED REFERENCES

1. Smolenskii, "New Seignettelectrics and Anti-Seignettelectrics," Sov. Phys. Uspekki, Vol. 62, 1957, pp. 58-100
2. Smolenskii and Agranovskaya, "The High Dielectric Constants of Cerates of Divalent Metals," Sov. Phys. - Tech. Phys., Vol. 1, 1956, p. 467
3. Maxwell, "Antimony-Doped Titanium Oxide Capacitors," Am. Ceram. Soc. Bull., Vol. 42, 1963, pp. 438-440
4. Novosil'tsev and Khodakov, "Dielectric Properties of Several Solid Solutions Which Contain Barium Titanate," Sov. Phys. - Tech. Phys., Vol. 1, 1956, pp. 306-318
5. Smolenskii, "Ferroelectric Phase Transformations in Solid Solutions of Perovskite Structure Formed in Some Binary Systems," Zhur. Neorg. Khim., Vol. 1, 1956, pp. 1402-1412
6. Smolenskii, Isupov, Agranovskaya, and Krainik, "New Ferroelectrics of Complex Composition IV," Sov. Phys. - Solid State, Vol. 2, 1961, pp. 2651-2654
7. Smolenskii, "New Ferroelectrics and Antiferroelectrics of the Oxy-octahedral Type," Acad. Sci. Bull. USSR, Vol. 20, 1956, pp. 149-160
8. Smolenskii, Isupov, and Agranovskaya, "Ferroelectric Properties of Solid Solutions in the System $\text{PbNb}_2\text{O}_6 - \text{BaNb}_2\text{O}_6 - \text{SrNb}_2\text{O}_6$," Sov. Phys. - Solid State, Vol. 1, 1959, 400-405
9. Smolenskii, Agranovskaya, Popov, and Isupov, "New Ferroelectrics of Complex Composition," Sov. Phys. - Tech. Phys., Vol. 3, 1958, pp. 1981-1982

10. Smolenskii and Agranovskaya, "Dielectric Polarization and Losses of Some Complex Compounds," Sov. Phys. - Tech. Phys., Vol. 3, 1958, pp. 1380-1382
11. Herczog, "Microcrystalline BaTiO_3 by Crystallization From Glass," J. Am. Ceram. Soc., Vol. 47, 1964, p. 107
12. Lockheed Missiles & Space Company, Proposal for Electrolytic Preparation of High Dielectric Thin Films, LMSC-896948, Sunnyvale, Calif., Mar 1963
13. Electrolytic Preparation of High Dielectric Thin Films, Contract No. NASW-765, Jun 1963
14. Sibert, "Electrochemical Oxidation of Titanium Surfaces," J. Electrochem. Soc., Vol. 110, 1963, p. 65
15. Lockheed Missiles & Space Company, Electrolytic Preparation of High Dielectric Thin Films, by Ring and Story, First Quarterly Report, 27 Sep - 27 Dec 1963
16. Ence and Margolin, J. Metals, Vol. 6, 1954, p. 346
17. Müller, Nicholson, and Francombe, "The Vapor Deposition of BaTiO_3 by a Grain to Grain Evaporation Method," J. Electrochem. Tech., Vol. 1, 1963, p. 158
18. Lockheed Missiles & Space Company, Electrolytic Preparation of High Dielectric Thin Films, by Hultquist and Sibert, 3rd Quarterly Report, 27 Dec 1963 - 27 Mar 1964

5.2 UNCITED REFERENCES

Aleksandrov, Lisker, and Friedberg, "Temperature Dependence of the Temperature Coefficient of the Dielectric Constant of Some Ionic Dielectrics," Fiz. Dielektrikov Sbornik, 1960, pp. 21-27; Discussion, pp. 37-38

Aleshin and Roy, "Crystal Chemistry of Pyrochlore," J. Am. Ceram. Soc., Vol. 45, 1962, pp. 18-25

- Baldwin, "How to Use Electronic Ceramics Better," Ceram. Ind., Vol. 71, 1958, No. 2, pp. 88-92; No. 3, pp. 132-136
- Barnett et al., Reduced TiO_2 Semiconductor Applications, Univ. of New Mexico, Albuquerque, N.M., Contract No. DA-49-186-502-ORD-779, Oct 1960
- Baxter and Hellicar, "Barium Titanate Dielectrics Containing Nickel Oxide," General Electric Co., Ltd., Britain, Patent 881,831, Appl. 27 Sep 1957
- Bokov and Myl'nikova, "Ferroelectric Properties of Single Crystals of New Compounds With Perovskite Structure," Fiz. Tverd. Tela, Vol. 2, 1960, pp. 2728-2732
- Breckenridge and Hosler, "Titanium Dioxide Rectifiers," J. Res. Natl. Bur. Std., Vol. 49, RP 2344, 1952, pp. 65-72
- Buganov and Khomutetskaya, "Additional Information Concerning the System of Solid Solutions $\text{PbTiO}_3 - \text{SrTiO}_3$," Izvest. Akad. Nauk. SSSR Ser. Fiz., Vol. 21, 1957, pp. 433-438
- Cherny, "Electric Properties of the System $\text{BaTiO}_3 - \text{CoZrO}_3$," Fiz. Dielektrikov Sbornik, 1960, pp. 385-392; Discussion pp. 429-431
- Chormunov, "Effect of Impurities in the Dielectric Permeability and the Piezoelectric Modulus of Seignette Salt," Sov. Phys. - Tech. Phys., Vol. 1, 1956, 319-321
- Coffeen, "Barium Titanate - Nickel Stannate Dielectrics," U.S. Patent 2,789,061, 16 Apr 1957
- Das Gupta, "High Dielectric Capacitors," U.S. Patent 2,801,181, 30 Jul 1957
- Day and Calis, "Ceramic Dielectric With High Dielectric Constant," U.S. Patent 2,776,898, 8 Jan 1957
- DeBretteville, Halden, Vasilos, and Reed, "Dielectric Studies in the System $\text{CdO} - \text{NO}_2\text{O}_5$," J. Am. Ceram. Soc., Vol. 40, 1957, pp. 86-89
- Eichbaum and Larssen, "Ceramic Dielectrics," Insulation, May 1963, pp. 267-286
- El'gard, "Dependence of Dielectric Constant and Losses of Ferroelectrics on the Electric Field Strength in the Range of 50 Cycles - 100 Kilocycles," Fiz. Tverd. Tela, Vol. 3, 1961, pp. 1485-1492

- El'gard, "Dependence of the Dielectric Constant and Dielectric Losses of Polarized Ferroelectrics on the Electric Field Intensity in the Frequency Range 50 Cycles - 100 Kilocycles," Fiz. Tverd. Tela, Vol. 3, 1961, pp. 1515-1521
- Fedulov and Venevtsev, "Structure and Dielectric Properties of Solid Solutions (Pb, Sr), (Ti, Zr)O₃," Fiz. Tverd. Tela, Vol. 3, 1961, pp. 3371-3375
- Fedulov, Venevtsev, Zhdanov, and Rez, "X-ray and Electric Studies of Specimens in the System PbTiO₃ - BaZrO₃, Metallografiya, Vol. 6, 1961, pp. 681-685
- Francombe and Lewis, J. Electronics, Vol. 2, 1957, pp. 387-403
- Francombe and Lewis, "Ferroelectric Ceramic Dielectric Materials," General Electric Co., Ltd., Britain, Patent 881,476, 1 Nov 1961; Appl. 17 Jan 1958
- Glaister and Woolner, "Relax: on Polarization Dielectrics. The System (Sr, Ba, Ca)TiO₃ - Bi₂O₃ - TiO₂, J. Electronic and Control, Vol. 6, 1959, pp. 385-396
- Gubkin and Skanavi, "New Electrets From Inorganic Dielectrics," Sov. Phys., JETP, Vol. 5, 1957, pp. 140-143
- Ikeda, "A Few Quarternary Systems of the Perovskite Type A++B⁴+O₃, Solid Solutions," J. Phys., Soc., Japan, Vol. 14, 1959, pp. 1286-1294
- Ishikawa and Sawada, "The Study of Substances Having the Ilmente Structure I," J. Phys. Soc., Japan, Vol. 11, 1956, pp. 496-501
- Isupov, "Dielectric Constant of Niobates and Tantalates of Bivalent Metals," Izvest. Akad. Nauk. SSSR, Ser. Fiz., Vol. 21, 1957, pp. 402-410
- Isupov and Kosyakov, "Dielectric Polarizations and Piezoelectric Properties of Ferroelectric Solid Solutions of Calcium, Strontium, and Barium Metaniobates in Lead Metaniobate," Sov. Phys. - Tech. Phys., Vol. 3, 1958, pp. 2002-2010
- Iteywang, "Barium Titanate as a Semiconductor With Blocking Layers," Solid State Electronics, Vol. 3, 1961, pp. 51-58
- Johnson, "Influence of Impurities on Electrical Conductivity of Rutile," J. Am. Ceram. Soc., Vol. 36, 1953, pp. 97-101
- Johnson and Weyl, "Influence of Minor Additions on Color and Electrical Properties of Rutile," J. Am. Ceram. Soc., Vol. 32, 1949, pp. 398-401

- Keler and Karpenko, "Conditions for the Formation of the Barium Titanates," Zhur. Neorg. Khim., Vol. 4, 1959, pp. 1125-1137
- Keler and Karpenko, "Interaction of BaCO_3 With TiO_2 and ZrO_2 During Heating," Zhur. Neorg. Khim., Vol. 5, 1960, pp. 668-675
- King, Schultz, Durban, and Duckworth, U.S. Atomic Energy Comm., BMI-1106, 1956, 40 pp.
- Khodakov, "Nonlinear Properties of Seignetteoelectrics at High Intensities of Field," Sov. Phys. - Tech. Phys., Vol. 1, 1956, pp. 47-55
- Khodakov, Sholokhovitch, Fesenko, and Kramarov, "The Preparation and the Dielectric and Optical Properties of Monocrystals of Solid Solutions of Barium and Strontium Titanates," Sov. Phys. - Doklady, Vol. 1, 1956, pp. 379-382
- Lewis and White, J. Electronics, Vol. 1, 1956, pp. 646-664
- Lisker, "Some Peculiarities in the Electrical Properties of Ceramic Dielectrics Based on Zirconium and Niobium Oxides," Zhur. Tekh. Fiz., Vol. 28, 1958, pp. 2428-2433
- McQuarrie, "The System (Ba, Ca, Pb) TiO_3 ," J. Am. Ceram. Soc., Vol. 40, 1957, pp. 35-41
- Mashkovich, "Nature of Conductivity of Titanium Containing Ceramic Materials," Trudy Gosudarst. Issledovatel, Elektrakeram. Inst., No. 2, 1957, pp. 92-100
- Maxwell, Freifelder, and Franklin, "Layerized High - Dielectric - Constant Capacitors," Electronic Design, Vol. 7, 1959, p. 70
- Mitsui and Westphal, "Dielectric and X-Ray Studies of $\text{Ca}_x\text{Ba}_{1-x}\text{TiO}_3$," Phys. Rev., Vol. 124, 1961, pp. 1354-1359
- National Academy of Science, National Research Council Publication 917, 1961, 302 pp.
- Nelson, Ceramic and Dielectric Properties of Lead Metaniobate Electrical Ceramics, Univ. Microfilms, Ann Arbor, Mich., L. C. Card No. Mic 58-5469, 105 pp; Diss. Abstr., Vol. 19, 1958, p. 1313

Novosil'tsev, Khodakov, Sholokhov, Fesenk, and Kramarov, "Growing and Investigation of Single Crystals of Ferroelectric Materials," Izvest. Akad. Nauk. SSSR, Ser. Fiz., Vol. 21, 1957, pp. 295-304

Popper, Ruddlesden, and Ingles, "Double Oxides With Layer Structures Related to Perovskite I," Trans. Brit. Ceram. Soc., Vol. 56, 1957, pp. 356-365

Schwarzback, "Dielectric Properties of the System BaO-TiO_2 ," Silikaty, Vol. 4, 1960, pp. 218-225

Sinyakov and Cherny, "Influence of Nonferroelectric Salt-Type Additives on Electrical Properties of Ferroelectric Salt-Type Ceramics," Nauch. Zapski, Dnepropetrovskii Gosndarst. Univ., Vol. 72, 1957, pp. 7-19

Skanavi and Matveeva, "New Dielectrics With Very High Dielectric Constant and Low Conductivity That do not Have Ferroelectric Properties," Zhur. Eksptl. i Teoret. Fiz., Vol. 30, 1956, pp. 1047-1051

Smolenskii, Isupov, and Agranovskaya, "Solid Solutions of Barium Metaniobate and Barium Metatantalate in Barium Titanate Which Have Seignetteoelectric Properties," Doklady Aked. Nauk SSSR, Vol. 113, 1957, pp. 1053-1056

Smolenskii, "New Ferroelectrics With a Complex Composition," Fiz. Dielektrikov, Tr. Vtoroi Vses. Konf., Akad. Nauk SSSR, Fiz. Inst., 1960, pp. 339-346

Smolenskii, Agranovskaya, and Isupov, "New Ferroelectrics of Complex Composition III Pb_2MgWO_6 , $\text{Pb}_3\text{Fe}_2\text{WO}_9$, and $\text{Pb}_2\text{FeTaO}_6$," Fiz. Tverd. Tela, Vol. 1, 1959, pp. 990-992

Smolenskii, Berkman, and Eidelkeend, "Ceramic Materials of High Mechanical Strength for High Frequency Uses," Steklo i Keranika, Vol. 6, 1949, pp. 17-22

Smolenskii, "Electrostriction Properties in Ceramic Seignetteoelectrics," Zhur. Tekhn. Fiz., Vol. 21, 1951, pp. 1045-1049

Smolenskii, "Seignetteoelectric Properties of Some Perovskite-Type Titanates and Zirconates of Bivalent Metals," Zhur. Tekhn. Fiz., Vol. 20, 1950, pp. 137-148

Smolenskii and Pasunkov, "Molecular Theory of Seignetteoelectric Bodies," Zhur. Eksptl. i Teoret. Fiz., Vol. 25, 1953, pp. 57-73

Smolenskii, "Tiglin, a Ceramic Material Having a Low Temperature Coefficient of Dielectric Permeability," J. Tech. Phys. (USSR), Vol. 15, 1945, pp. 173-181

Smolenskii and Rozhgachev. "Seignetteoelectric Properties of Solid Solutions in the System Barium Titanate - Strontium Titanate, Zhur. Tekh. Fiz., Vol. 24, 1954, pp. 1751-1760

Smolenskii, Isupov, and Agranovskaya, "New Group of Ferroelectrics (With a Laminated Structure)," Fiz. Tverd. Tela, Vol. 1, 1959, pp. 169-170

Smolenskii, Agranovskaya, and Popov, "Mechanism of Polarization in Solid Solutions of $Pb_3NiNb_2O_9 - Pb_3MgNb_2O_9$," Fiz. Tverd. Tela, Vol. 1, 1959, pp. 167-168

Smolenskii, Isupov, and Agranovskaya, "New Ferroelectrics of Complex Composition of the Type $A_2^{++}(B_I^{+++}B_{II}^{5+})O_6$," Fiz. Tverd. Tela, Vol. 1, 1959, pp. 170-171

Smolenskii, "Phase Transitions in Seignetteoelectric Solid Solutions Based on Strontium Purotantalate," Doklady Acad. Nauk SSSR, Vol. 113, 1957, 803-805

Smolenskii and Isupov, "Phase Changes of Certain Solid Solutions Having Electrical Properties of Rochelle Salt," Doklady Akad. Nauk SSSR, Vol. 96, 1954, pp. 53-54

Smolenskii, "Seignetteoelectric Properties of Some Crystals," Doklady Akad. Nauk SSSR, Vol. 85, 1952, pp. 985-987

Smolenskii and Pasunkov, "The Theory of Seignetteoelectricity," Doklady Akad. Nauk SSSR, Vol. 79, 1951, pp. 431-434

Smolenskii, Karamushev, and Rozhgachev, "Seignetteoelectric Properties of Some Solid Solutions," Doklady Akad. Nauk SSSR, Vol. 79, 1951, pp. 53-56

Smolenskii and Kozhevneekov, "The Problem of the Origin of Seignetteoelectricity," Doklady Akad. Nauk SSSR, Vol. 76, 1951, pp. 519-522

Smolenskii, "New Seignetteoelectric Substances," Doklady Akad. Nauk SSSR, Vol. 70, 1950, pp. 405-408

Smolenskii, Agranovskaya, Kalinina, and Fedotova, "Signetoelectric Properties of Solid Solutions: $(\text{Pb}, \text{Ba})\text{SnO}_3$, $\text{Pb}(\text{Ti}, \text{Sn})\text{O}_3$, and $\text{Pb}(\text{Zr}, \text{Sn})\text{O}_3$," Zhur. Tekh. Fiz., Vol. 25, 1955, pp. 2134-2142

Smolenskii and Gurevich, "Ferromagnetic Semiconductors," Poluprovod v Nauki i Tekh. Akad. Nauk SSSR Inst. Poluprovod, Vol. 2 (A. F. Ioffe, ed.) Moscow: 1zd. Akad. Nauk SSR, 1958, pp. 349-424

Smolenskii and Isupov, "Seignetoelectric Substances," Poluprovod. v Nauki i Tekh. Akad. Nauk SSSR Inst. Poluprovod. Z. (A. F. Ioffe, ed.) Moscow: 1zd. Akad. Nauk SSSR, 1958, pp. 425-462

Smolenskii and Agranovskaya, "Dielectric Polarization of a Series of Compounds of Complex Composition," Fiz. Tverd. Tela, Vol. 1, 1959, pp. 1562-1572

Smolenskii, "Survey of the Results of Recent Investigations of Ferroelectric Materials," Acad. Sci., Vol. 21, 1957, pp. 235-265

Smolenskii, Isupov, and Agranovskaya, "High Dielectric Constants of Niobates and Tantalates of Divalent Metals," Sov. Phys. Doklady, Vol. 1, 1956, pp. 300-302.

Smolenskii, Isupov, and Agranovskaya, "Ferroelectrics of the Oxygen-Octahedral Type With Layered Structure," Sov. Phys. - Solid State, Vol. 3, 1961, pp. 651-655

Smolenskii, Tszun, and Stankevich, "Influences of Electron Diffusion of the Radio-Frequency Dispersion or the Magnetic Permeability of Ferrites With a Garnet Type Structure," Sov. Phys. - Solid State, Vol. 3, 1961, pp. 486-489

Smolenskii, Tsung, and Sher, "Garnet-Type Structure Ferromagnetics With High Initial Permeability," Sov. Phys. - Solid State, Vol. 3, 1961, pp. 1314-1316

Smolenskii, Isupov, Kranik, and Agranovskaya, "Concerning the Coexistence of the Ferroelectric and Ferromagnetic States," Acad. Sci., USSR, Vol. 25, 1961, pp. 1345-1350

Smolenskii and Andreer, "Investigation of Ferrimagnets With the Structure of Magnetoplumbite and Garnet in Strong Pulse Magnetic Fields," Acad. Sci. USSR, Vol. 25, 1961, pp. 1405-1411

Smolenskii, Polyakov, and Yudin, "Investigation of the Magnetic Properties of Some Ferromagnetics With the Structure of Perovskite and Garnet," Acad. Sci. USSR, Vol. 25, 1961, pp. 1408-1411

Smolenskii, Chang, and Sher, "Frequency and Temperature Dependences of the Initial Permeability of Ferrites With the Garnet Structure," Acad. Sci. USSR, Vol. 25, 1961, pp. 1414-1418

Smolenskii and Agranovskaya, "Dielectric Polarization of a Number of Complex Compounds," Sov. Phys. - Solid State, Vol. 1, 1960, pp. 1429-1437

Smolenskii, Isupov, and Agranovskaya, "Ferroelectric Substitutional-Defect Solid Solutions," Sov. Phys. - Solid State, Vol. 1, 1960, pp. 1438-1445

Smolenskii, "On the Occurrence of Spontaneous Polarization in Crystals," Sov. Phys. - Tech. Phys., Vol. 2, 1957, pp. 1652-1656

Smolenskii, Isupov, Agranovskaya, and Sholokhova, "Nonferroelectric Phase Transitions in Solid Solutions Formed in the Systems (Ca, Sr) (Ti, Zr)O₃ and Na(Nb, Ta)O₃," Sov. Phys. - Tech. Phys., Vol. 2, 1957, pp. 2351-2356

Smolenskii, Isupov, Agranovskaya, and Popov, "Ferroelectrics With Diffuse Phase Transitions," Sov. Phys. - Solid State, Vol. 2, 1961, pp. 2584-2594

Sprague Electric Co., "Barium Titanate Dielectric," Britain, Patent 892,547, 28 Mar 1962, Appl. 3 Nov 1960

Suchoff, "Ferroelectric Barium Titanate Coatings," U.S. Patent 3,002,861, Appl. 7 Jun 1957

Verbitskaya, Gindin, and Prokhratilov, "Structural and Electric Properties of the Ferroelectric Systems: BaTiO₃ - BaZrO₃, BaTiO₃ - BaSnO₃, BaTiO₃ - ZrO₂ and BaTiO₃ - SnO₂," Fiz. Tverd. Tela, Akad. Nauk SSSR Sbornik State, Vol. 1, 1959, pp. 180-189

Verwey, "Oxide Semi-Conductors," Semiconducting Materials (Proc. Conf. Univ. Reading, Eng. 1, 1951, pp. 151-161

Verwey, et al., Controlled-Valency Semiconductors, Philips Res. Rept., Vol. 5, 1950, pp. 173-187

von Hippel, Kalnajs, and Westphal, Dipoles and Charge Carriers in Rutile, Laboratory for Insulation Research, Mass. Inst. Technology, Cambridge, Tech. Report No. 164, Jun 1961, 32 pp.

Winogradow and Wida, "Ceramics for Condensers With a Temperature Coefficient of the Dielectric Constant $TkE = 150 \pm y_0 \times 10^{-6}/^{\circ}C$," Szklo i Ceram., Vol. 11, 1960, pp. 108-114

Zhukov, "Effect of Isomorphous Impurities on the Piezoelectric Properties of Barium Titanate," Trudy, Voronezh. Gosudarst. Univ., Vol. 60, No. 3, 1957, pp. 13-21